low-temperature spectrum of c-C_5H_9-OD shows significant changes in peak intensity, confirming that some of the various forms result from hydrogen bonding.

We also examined sulfolane, $SO_2(CH_2)_4$ (mp +27 °C), for which X-ray results have been reported.[8] We find that each peak in the melt (C1 and C2) splits into two peaks with a ratio of about 2/1 below +10 °C. These must come from different conformers, as hydrogen bonding is not a factor. Solid cyclopentanone also gives two peaks from all but one carbon.

Cyclopentanol, cyclohexanol, and sulfolane crystallize from the liquid into plastic crystals, in which the molecules, because of their globular shapes, still retain the freedom to rotate.[9] The NMR decoalescence occurs close to the transition temperature from plastic to nonplastic forms.[10] Above coalescence, the spectrum is like that of the isotropic liquid. At the plastic to nonplastic transition temperature, the spectrum passes through a dynamic decoalescence to give a spectrum characteristic of the solid. Sulfolane and cyclopentanone in the nonplastic solid contain two distinct, probably conformational environments for each carbon. Cyclopentanol and cyclohexanol contain numerous environments for C2 and C3 brought about by hydrogen bonding. For these materials, which in general cannot give crystal structures, the NMR spectra can provide details about the forms present in the nonplastic phase.

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How Do Reaction Mechanisms Change? Appearance of Concerted Pericyclic Elimination for the Reaction of Cumyl Derivatives

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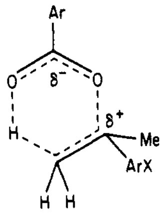
We report that destabilization of the carbocation intermediate of the stepwise solvolysis reaction of tertiary cumyl derivatives, $XArC(Me)_2Y$, by the addition of electron-withdrawing ring substituents, leads to a change in mechanism to *concerted pericyclic* elimination in which intramolecular proton transfer to the leaving group, Y = $ArCO_2$ or Cl, is concerted with C–Y bond cleavage (see **1**).



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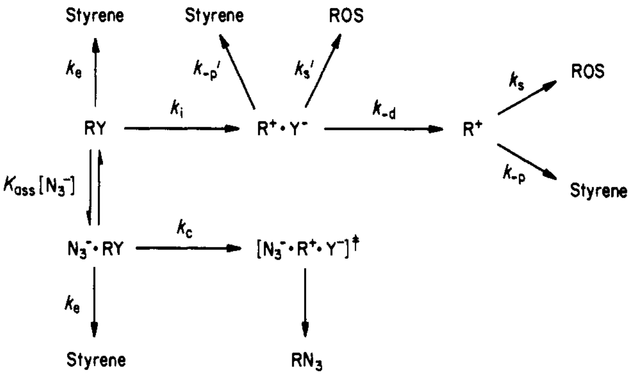
In 50:50 (v/v) trifluoroethanol/water, cumyl 4-nitrobenzoates, $XArC(Me)_2OPNB$, with $\sigma_x^+ < -0.08$, solvolyze by a stepwise S_N1 (or $D_N + A_N$)[1] mechanism through liberated carbocation intermediates that are captured by solvent with rate constants $k_s = 10^7\text{–}10^9\ s^{-1}$.[2] There is very little ($\leq 1\%$)[3] deprotonation of the carbocation intermediate to give the corresponding α-methylstyrene (k_{-p}, Scheme I).[4] For $-0.08 \leq \sigma_x^+ \leq 0.12$, $k_s = 4 \times 10^9\text{–}3 \times 10^{10}\ s^{-1}$,[2] and the carbocation reacts with solvent largely before diffusional separation of the carbocation–leaving group ion pair can occur ($k_s' \approx k_{-d}$, Scheme I).[5] These reactions are accompanied by a larger amount (4–5%) of elimination, which may arise from proton abstraction by the leaving group within an ion pair (k_{-p}', Scheme I).[5–7]

Scheme I



Further destabilization of the carbocation intermediate leads to substantially larger yields of the α-methylstyrenes (Table I). The yields of α-methylstyrene for cumyl derivatives with $\sigma_x^+ \geq 0.34$ are 2–3-fold larger for the more basic pentafluorobenzoate compared with a chloride leaving group, and the fraction of elimination, f_{elim}, increases dramatically (up to 30% for 4-$NO_2ArC(Me)_2OPFB$ or 3,5-$(CF_3)_2ArC(Me)_2Cl$) as the aromatic substituent X is made more electron withdrawing. For $XArC(Me)_2Y$ with $\sigma_x^+ \geq 0.34$, the addition of 0.50 M NaN_3 leads to 20–30% yields of the azide adducts RN_3 by a preassociation mechanism (K_{ass} and k_c, Scheme I) in which azide ion provides no *assistance* to the reaction of the substrate ($k_i = k_c$).[2,8] Product analysis[4] showed that the azide adduct is formed solely at the expense of the solvent adducts ROS: the yield of α-methylstyrene is *independent* of $[N_3^-]$. This shows that solvolysis and elimination occur by *separate* pathways (k_i and k_e, Scheme I) and *not* by partitioning of a common ion pair intermediate. The reaction of the encounter complex $N_3^-\cdot RY$ to give the azide adduct RN_3 would be expected to lead to a decrease in the yields of *all* products formed from reaction of free RY, including any derived from intimate or "tight" ion pairs. Therefore, the independence of the yield of α-methylstyrene of $[N_3^-]$ requires that elimination also occur from the complex $N_3^-\cdot RY$, with a rate constant (k_e) equal to that for elimination from RY alone. The formation of α-methylstyrene from $N_3^-\cdot RY$ *must* be by a concerted mechanism, because the triple ion complex $[N_3^-\cdot R^+\cdot Y^-]$ is too unstable to exist as an intermediate.[9]

The following structure–reactivity effects are consistent with the formation of α-methylstyrene from 3-F-, 4-NO_2-, and 3,5-$(CF_3)_2$-substituted cumyl pentafluorobenzoates and chlorides by *concerted* elimination at the neutral substrate (k_e, Scheme I) that occurs both in the presence and in the absence of an associated

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[4] Product yields were determined by HPLC.

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[9] The estimated rate constant for collapse of $[N_3^-\cdot 3,5\text{-}(CF_3)_2ArC(Me)_2^+\cdot Cl^-]$ to give RN_3 is $k_{nuc} \approx 10^{19}\ s^{-1}$.[2] Therefore, this species has a lifetime much shorter than the time for a single bond vibration ($\sim 10^{-13}$ s) so that it cannot exist as an intermediate.[2,8] Even if it were to form, then it would give only RN_3, because the barrier for addition of the strong nucleophile N_3^- to the carbocation is much smaller than that for deprotonation to give α-methylstyrene.

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Table I. Rate Constants for Solvolysis and Elimination and Yields of α-Methylstyrene for Reaction of Ring-Substituted Cumyl Derivatives, XArC(Me)$_2$Y, in 50:50 (v/v) Trifluoroethanol/Water[a]

X	Y	$\sigma_x^{+\,b}$	k_{obsd},[c] s^{-1}	f_{elim}[d]	k_{solv},[e] s^{-1}	k_{elim},[f] s^{-1}
3-F	Cl	0.34	0.12	0.044	0.11	5.3×10^{-3}
	OPFB[g]		2.60×10^{-5}[h]	0.15	2.2×10^{-5}	3.9×10^{-6}
	d_6-OPFB[i]		1.81×10^{-5}[h]	0.050	1.7×10^{-5}	9.1×10^{-7}
4-NO$_2$	Cl	0.78	2.34×10^{-4}	0.15	2.0×10^{-4}	3.5×10^{-5}
	OPFB			0.30		
3,5-(CF$_3$)$_2$	Cl	0.95[j]	3.20×10^{-5}	0.29	2.3×10^{-5}	9.3×10^{-6}

[a] At 25 °C and ionic strength 0.50 (NaClO$_4$). [b] Reference 19. [c] Determined spectrophotometrically for Y = Cl by following either the disappearance of the chloride (3-F at 250 or 270 nm, 3,5-(CF$_3$)$_2$ at 265 or 280 nm) or the appearance of the α-methylstyrene (4-NO$_2$ at 320 nm). [d] Fractional yield of α-methylstyrene, determined by HPLC analysis. [e] $k_{obsd}(1 - f_{elim})$. [f] $k_{obsd}(f_{elim})$. [g] Pentafluorobenzoate leaving group. [h] Determined by following the disappearance of the substrate by HPLC. [i] Data for 3-FArC(CD$_3$)$_2$OPFB. [j] Takeuchi, K.; Kurosaki, T.; Okamoto, K. *Tetrahedron* **1980**, *36*, 1557-1563.

azide ion. They are very hard to rationalize by deprotonation within an unselective carbocation-leaving group intimate or solvent-separated ion pair (k_{-p}').

(1) There is a large kinetic β-deuterium isotope effect on the elimination reaction of 3-FArC(CL$_3$)$_2$OPFB of $(k_{6H}/k_{6D})_{elim}$ = 4.3 (Table I). For an ion pair mechanism, deprotonation competes with the rapid diffusional separation of the ion pair ($k_{-d} \approx 10^{10}$ s^{-1})[5] and/or capture of the ion pair by solvent ($k_s' \approx 10^{11}$ s^{-1} for 3-FArC(Me)$_2^+$),[2] so that the barrier to proton transfer must also be very small. It is difficult to reconcile the large isotope effect with an extremely rapid proton transfer reaction in which little discrimination between abstraction of a proton and of a deuteron is expected.

(2) The values of k_{solv} and k_{elim} for XArC(Me)$_2$Cl are correlated by $\rho^+_{solv} = -6.1$ and $\rho^+_{elim} = -4.6$. Deprotonation and capture by solvent of a highly reactive and unselective ion pair should have early carbocation-like transition states of very similar polarity. Therefore, the substantial difference in these ρ values is difficult to rationalize by a mechanism that involves the partitioning of an ion pair intermediate.

(3) Similarly, there is a smaller sensitivity to solvent ionizing power (Y)[10] for k_{elim} (m_{elim} = 0.7) compared with k_{solv} (m_{solv} = 1.0) for reaction of 4-NO$_2$ArC(Me)$_2$Cl when the solvent is varied from 10:90 (v/v) MeOH/H$_2$O to 90:10 (v/v) MeOH/H$_2$O.

There is good evidence that the concerted elimination at the neutral substrate is *not* a bimolecular E2 reaction with an E1-like transition state[11] in which solvent assists as a general base,[12] because acetate (0.50 M) or trifluoroethoxide (0.10 M) ions do not catalyze elimination for cumyl derivatives with $\sigma_x^+ \geq 0.34$. If these strong bases do not promote elimination, then it is unlikely that the much more weakly basic solvent assists the reaction. We conclude that the elimination at 3-F-, 4-NO$_2$-, and 3,5-(CF$_3$)$_2$-substitituted cumyl pentafluorobenzoates and chlorides in 50:50 (v/v) TFE/H$_2$O proceeds by a *concerted unimolecular* mechanism with a carbocation-like transition state, *without* an intermediate, in which the leaving group acts as an intramolecular general base for proton abstraction (see **1**).

These reactions are an example of "pericyclic" E$_i$[13] (cyclo-D$_E$D$_N$A$_n$)[1] elimination (or retro-"ene" reaction[14]). Such reactions (e.g., pyrolytic eliminations of acetic acid or HCl) are well documented, not only in the gas phase[15] but also in nonpolar aprotic solvents,[15] where the formation of ionic intermediates is unfavorable. A good ionizing solvent is usually *assumed* to lead to a stepwise mechanism,[15a] and elimination reactions at tertiary carbon are often proposed to proceed through ion pair intermediates.[16-18] Our results show that, even in polar solvents, the concerted pericyclic mechanism is followed when the intermediate of the stepwise reaction becomes very unstable. This E$_i$ mechanism and its stepwise unimolecular counterpart are distinguished by the existence of an intermediate for the latter; the former proceeds through a transition state that *resembles* the intermediate of the stepwise reaction.[8]

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[2 + 2] Cyclodimerization of Ligated Benzene following Reductive Activation of $[Mn(\eta^6\text{-}C_6H_6)(CO)_3]^+$ To Give $[\{Mn(CO)_3\}_2\{\mu(\eta^4\text{-}C_6H_6\text{-}\eta^4\text{-}C_6H_6)\}]^{2-}$

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Orbital symmetry control of thermal and photochemical cycloaddition and dimerization of benzene has been extensively investigated both theoretically and experimentally.[1] One conclusion is that dimerization of benzene to *cis-anti-cis*-4a,4b,8a,8b-tetrahydrobiphenylene is photochemically allowed (from b$_{1u}$ and charge-transfer excited states),[1,2] but dimerization has never been observed under thermal or photochemical conditions. Tetrahydrobiphenylene has also, however, been of interest as an isomer of 12-annulene[3] and has been synthesized.[4] We now report (Scheme I; this includes selected ^{13}C data for some of the new compounds) that reductive activation of the benzene in $[Mn(\eta^6\text{-}C_6H_6)(CO)_3]^+$ leads to dimerization to give [{Mn-

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